and $Fe(H_2O)_6^{3+}$ in Cl^- solution also produces exclusively $CrCl^{2+}$,[16] which could arise from either of the mechanisms outlined above for Eu^{2+}. Previous studies on Eu^{2+} reactions[10] have suggested inner-sphere reaction mechanisms, and we think the present work provides a strong indication that inner-sphere mechanisms are involved.

The theory of Marcus[39] on electron-transfer reactions has been applied quite successfully, especially by Sutin and co-workers[11,40] to reactions between metal ions such as those considered here. Although the theory was developed from a model of an outer-sphere reaction, attempts have recently also been made to extend its applicability to other situations. The predicted rate constant can be calculated, as shown by Sutin,[40] from exchange rates and standard potentials. Unfortunately only a lower limit has been determined for the $Eu^{2+,3+}$ exchange rate in perchlorate solution.[12] The prediction on this basis is $k_0 < 2.6 \times 10^6\ M^{-1}\ sec^{-1}$; this is not inconsistent with our experimental result $k_0 = 6.77 \times 10^3\ M^{-1}\ sec^{-1}$ at 25°. The comparison in this particular instance is not a fruitful one in view of the unknown exchange rate constant.

Table VII. Relative Reactivities[a] of Various Dipositive Metal Ion Reducing Agents toward Iron(III) Complexes

	$k_{Fe(III)}/k_{Fe(H_2O)_6^{3+}}$			
	Reducing agent			
	Cr^{2+}	V^{2+}	Fe^{2+}	Eu^{2+}
	Mechanism			
	Inner	Outer	Inner	
$Fe(H_2O)_6^{3+}$	1.0	1.0	1.0	1.0
$(H_2O)_5FeOH^{2+}$	1.4×10^3	≤ 22	8.2×10^2	1.35×10^3
$Fe^{3+} + Cl^-$	10	≤ 4	. . .[b]	1.8
$(H_2O)_5FeCl^{2+}$	1×10^3	26	≤ 3.8[c]	0.51×10^3
Ref	16	36	38	This work

[a] Relative rates at $\mu = 1.00\ M$ and 25°, except Eu^{2+}, 1.6°, and Fe^{2+}, 20°. [b] For the purposes of this table, the chloride catalysis has arbitrarily been assumed to occur by the path involving the inner-sphere $FeCl^{2+}$ complex. [c] The ratio of rates is 7.6, but the inner-sphere path contributes 50% at most to the chloride catalysis (*i.e.*, there is a "direct" exchange path that does not find a parallel in the systems where net reaction occurs).[38]

Acknowledgment. We are grateful to Drs. N. Sutin and T. W. Newton for their helpful comments and suggestions.

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Ethylenebis(diphenylphosphine) Complexes of Iron and Cobalt. Hydrogen Transfer between the Ligand and Iron Atom

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Abstract: Reduction of iron(III) acetylacetonate and cobalt(III) acetylacetonate with ethoxydiethylaluminum in the presence of ethylenebis(diphenylphosphine) (EDP) gives $Fe(EDP)_2 \cdot C_2H_4$ and $HCo(EDP)_2$, respectively. Ultraviolet irradiation of $Fe(EDP)_2 \cdot C_2H_4$ results in the formation of $HFe(C_6H_4PPh \cdot CH_2CH_2 \cdot PPh_2)(EDP)$, in which hydrogen transfer from a phenyl group of the ligand to the iron atom takes place. The hydrogen atom of the Fe–H bond of the iron hydride is labile and returns to the original ligand with ease. The iron hydride is converted into $Fe(EDP)_2 \cdot C_2H_4$ under ethylene pressure. Reaction of the iron hydride with deuterium chloride affords $DFeCl(EDP)_2$ and $HFeCl(C_6H_4DPPh \cdot CH_2CH_2 \cdot PPh_2)(EDP)$ in a ratio of 80:20. The iron complexes $Fe(EDP)_2 \cdot C_2H_4$ and $HFe(C_6H_4PPh \cdot CH_2CH_2 \cdot PPh_2)(EDP)$ react with hydrogen at atmospheric pressure to give $H_2Fe(EDP)_2$.

There have been several reports on the synthesis of 1,4-dienes by the reaction of 1,3-dienes with ethylene in the presence of catalysts consisting of some transition metal compounds and organoaluminum compounds.[1,2] Recently, it has been found that catalysts consisting of iron or cobalt compounds, ditertiary phosphines, and organoaluminum compounds show an excellent activity for this reaction.[3,4] Organoaluminum compounds in these catalyst systems are assumed to act as a reducing agent and as a Lewis acid. With the object of acquiring knowledge about the reducing property of the organoaluminum compounds and clarifying the active species of the catalysts, we have investigated the reaction of iron(III) acetylacetonate and cobalt(III) acetylacetonate with ethoxydiethylaluminum in the presence of ethylenebis(diphenylphosphine). The present paper describes the preparation and characterization of ethylenebis(diphenylphosphine) complexes of low-valent iron and cobalt. In the course of the study of the reactivities of the iron complex, we have found a reversible hydrogen transfer between the ligand and the iron atom.

Results and Discussion

Complexes of Iron. Reaction of iron(III) acetylacetonate with ethoxydiethylaluminum in the presence of ethylenebis(diphenylphosphine) (hereafter EDP) in ethyl ether at 0° gave a red complex **1a** in 85% yield. Repeated recrystallization of this complex from benzene–

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[1] (a) G. Hata, *J. Am. Chem. Soc.*, 86, 3903 (1964); (b) G. Hata and D. Aoki, *J. Org. Chem.*, 32, 3754 (1967).

[2] T. J. Kealy, French Patent 1,388,305 (1964).

[3] M. Iwamoto and S. Yuguchi, *J. Org. Chem.*, 31, 4290 (1966).

[4] A. Miyake, G. Hata, M. Iwamoto, and S. Yuguchi, "Proceedings of the 7th World Petroleum Congress, Panel Discussion," Vol. 22, 1967, p 37.

ether resulted in the formation of a violet complex **1b**, and so no satisfactory purification of **1a** could be achieved. It was found that the presence of a small amount of ethylenebis(diphenylphosphine) accelerated this transformation. The latter complex was identified as $Fe(EDP)_2 \cdot C_2H_4$ by means of elemental analysis, infrared spectroscopy, and chemical reactions. Treatment of **1b** with iodine gave $FeI_2(EDP)$ and ethylenebis(diphenylphosphine) with liberation of an equivalent amount of ethylene. A molecular weight measurement showed that **1b** was monomeric in benzene. From the fact that ultraviolet irradiation of **1a** and **1b** liberated ethylene to afford the same complex, as described later, they are considered to be isomeric. The similarity of their infrared spectra suggests that they are geometrical isomers. The spectra of **1a** and **1b** in Nujol mull showed absorptions due to C–H stretching vibration of coordinated ethylene at 3019 and 3016 cm^{-1}, respectively. These complexes are quite sensitive to air, especially in solution. Reduction of iron(III) acetylacetonate could proceed through homolytic fission of iron–carbon bonds of an ethyliron intermediate, and the coordinated ethylene molecule is probably derived from this intermediate. Evolved gas in the preparation consisted mainly of ethane. A similar formation of an ethylene–metal π complex has been observed in the reduction of nickel(II) acetylacetonate with ethoxydiethylaluminum in the presence of triphenylphosphine.[5]

$$Fe(EDP)_2 \cdot C_2H_4 + I_2 \longrightarrow FeI_2(EDP) + EDP + C_2H_4 \quad (1)$$

Ultraviolet irradiation of **1a** or **1b** resulted in the formation of an orange-brown complex **2**, with liberation of an equivalent amount of ethylene. The same complex was formed also by heating **1a** or **1b** with a small amount of the mother liquor obtained in the preparation of **1a**. Treatment of **2** with iodine gave $FeI_2(EDP)$ and ethylenebis(diphenylphosphine). The complex **2** was monomeric in benzene. From these facts, **2** might be expected to be $Fe(EDP)_2$. However, the infrared and nmr spectra showed the presence of an Fe–H bond. This observation indicates that hydrogen transfer from the coordinated ligand to the iron atom takes place. The nmr spectrum (Figure 1) showed a multiplet centered at τ 24.2, which can be ascribed to an ion hydride. The constancy of the splitting within the multiplet at 60 and 100 Mc indicates that the splitting is due to coupling of the hydrogen nucleus with the phosphorus nuclei. The ratio (8:1) of the integrated intensity of $>PCH_2CH_2P<$ to that of Fe–H in the nmr spectrum can be reasonably explained by assuming that **2** has the following structure, in which the iron atom is inserted into a C–H bond of a phenyl group of the coordinated ligand.

$$HFe(C_6H_4PPh \cdot CH_2CH_2 \cdot PPh_2)(EDP)$$

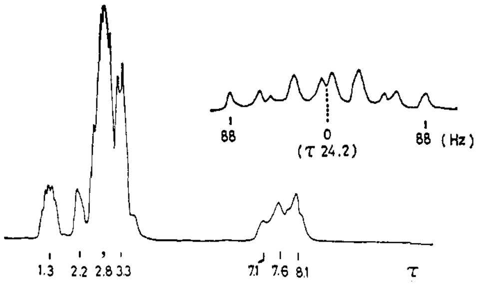

Figure 1. Nmr spectrum (100-MHz) of $HFeC_6H_4PPh \cdot CH_2CH_2 \cdot PPh_2)(EDP)$ in C_6D_6.

If the hydrogen transfer takes place from the $>PCH_2$-$CH_2P<$ group to the iron atom, the ratio should be 7:1. The infrared spectrum also showed a characteristic absorption due to an Fe–H stretching vibration at 1893 cm^{-1}. This complex showed a sharp absorption at 1554 cm^{-1}, which was not observed in the complexes **1a** and **1b**. The position of attachment of the iron atom on the benzene ring has not been confirmed, though from the steric requirement it may probably be an *ortho* position. An intense band at 728 cm^{-1}, which is absent in ethylenebis(diphenylphosphine) and the complexes **1a** and **1b**, may be assigned to the C–H out-of-plane deformation mode of an *ortho*-disubstituted benzene.[6] It was reported that one of the *o*-hydrogen atoms of the ligand of dichlorotris(triphenylphosphine)ruthenium(II) was quite near to the central metal atom (2.59 Å).[7] A similar observation was also made in a five-coordinated iridium complex, $[Ir(CO)(EDP)_2]Cl$.[8] The formation of a bond between the metal atom and an *o*-carbon atom of an aromatic ring of a ligand has been previously reported in the reaction of aromatic azo compounds with dicyclopentadienylnickel,[9] iron carbonyl,[10] and platinum and palladium salts,[11] although in these cases there is no migration of the *o*-hydrogen atoms to the metal atoms. The first report of hydrogen transfer from a coordinated ligand to a metal atom was made in an ethylenebis(dimethylphosphine) complex of ruthenium, $HRu(CH_2PMe \cdot CH_2CH_2 \cdot PMe_2)(Me_2P \cdot CH_2CH_2 \cdot PMe_2)$.[12] However, such a hydrogen transfer was not observed in the iron complex $Fe(Me_2P \cdot CH_2CH_2 \cdot PMe_2)_2$.[13] In a recent communication, Bennett has reported the transfer of an *o*-hydrogen atom of a coordinated ligand to the central metal atom on heating chlorotris(triphenylphosphine)iridium(I).[14]

Treatment of **2** with an equivalent amount of hydrogen chloride gave a violet complex, *trans*-$[HFeCl(EDP)_2]$. The *trans* configuration was supported by the nmr spectrum which showed a triplet with intensities approximately in a ratio of 4:6:4 at τ 39.2. The *trans* isomer should show a quintet with 1:4:6:4:1 intensity pattern by the four equivalent phosphorus nuclei. Three strong signals were observed since the outer signals were within the noise level. The *trans* configuration was also supported by a small phosphorus–hydrogen coupling constant (J_{PH} = 47 cps). The infrared spectrum of this complex did not show any detectable absorption due to an Fe–H stretching vibration, although an Fe–H stretching absorption is

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[13] J. Chatt and H. R. Watson, *ibid.*, 2545 (1962).

[14] M. A. Bennett and D. L. Milner, *Chem. Commun.*, 581 (1967).

usually observed in this type of hydride complex.[15] From the fact that the infrared spectrum of the deuterated complex, $DFeCl(EDP)_2$, is identical with that of the nondeuterated one, it seems likely that this absorption is too weak to be detected.

$$HFe(C_6H_4PPh\cdot CH_2CH_2\cdot PPh_2)(EDP) + HCl \longrightarrow HFeCl(EDP)_2 \quad (2)$$

$$Fe(EDP)_2\cdot C_2H_4 + H_2 \longrightarrow H_2Fe(EDP)_2 + C_2H_4 \quad (3)$$

$$HFe(C_6H_4PPh\cdot CH_2CH_2\cdot PPh_2)(EDP) + H_2 \longrightarrow H_2Fe(EDP)_2 \quad (4)$$

Hydrogen reacted with **1b** or **2** at 60∼70° and atmospheric pressure to give $H_2Fe(EDP)_2$, the former reaction being accompanied by liberation of ethylene. The reaction of hydrogen with **1b** was accelerated by ultraviolet irradiation. This dihydride crystallized as a solvate with a molecule of benzene or xylene, or with two molecules of toluene. It has been reported that ethylenebis(diphenylphosphine) complexes of Ru(II) and Os(II) have a great tendency to crystallize as solvates.[16,17] Solvating aromatic molecules affected the Fe–H stretching frequency of the dihydride (Table I). The Fe–H stretching absorptions of these solvated complexes appear at higher wave numbers by about 100 cm^{-1} than that of the reported iron dihydride complex, *trans*-$[H_2Fe\{o\text{-}C_6H_4(PEt_2)_2\}_2]$.[15] Owing to the poor solubility of the dihydride, its nmr spectrum in deuterated benzene did not show signals assignable to Fe–H protons. Treatment of the dihydride with iodine gave $FeI_2(EDP)$ with evolution of an equivalent amount of hydrogen.

Table I. Iron Dihydride Complexes

Complex	Mp (dec), °C	ν_{Fe-H},[a] cm^{-1}
$H_2Fe(EDP)_2\cdot C_6H_6$	219–220	1840
$H_2Fe(EDP)_2\cdot 2C_7H_8$	229–230	1835
$H_2Fe(EDP)_2\cdot C_8H_{10}$	234–236	1828

[a] In Nujol mull.

The hydrogen atom of the Fe–H bond of **2** was found to be quite labile and to return to the original ligand with ease. The complex **2** was converted into **1b** under ethylene pressure (60 kg/cm^2) at 80°. It is noteworthy that the hydrogen transfer between the metal atom and the ligand occurs reversibly.

$$HFe(C_6H_4PPh\cdot CH_2CH_2\cdot PPh_2)(EDP) \underset{-C_2H_4}{\overset{+C_2H_4}{\rightleftharpoons}} Fe(EDP)_2\cdot C_2H_4 \quad (5)$$

The predominant return of the hydrogen atom of the Fe–H bond of **2** to the original ligand was also observed in the reaction with hydrogen chloride. A deuterated complex prepared by the reaction of **2** with deuterium chloride was analyzed by nmr and mass spectroscopy. The fission of the iron–carbon bond by deuterium chloride should give an iron hydride complex with a deuterated ligand (A). On the other hand, the return of the hydrogen atom of the Fe–H bond to the original ligand should give an iron deuteride complex (B). A peak height of an Fe–H signal in the nmr specturm of the deuterated complex was one-fourth of that of the nondeuterated one. A mass spectrum of ethylenebis(diphenylphosphine) obtained by decomposition of the deuterated complex showed that it contained a mole fraction of 0.10 of monodeuterated ethylenebis(diphenylphosphine). Both results show good agreement and indicate that the deuterated complex consists of 20% A and 80% B.

$$HFe(C_6H_4PPh\cdot CH_2CH_2\cdot PPh_2)(EDP) + DCl \longrightarrow \underset{A,\ 20\%}{HFeCl(C_6H_4DPPh\cdot CH_2CH_2\cdot PPh_2)(EDP)} + \underset{B,\ 80\%}{DFeCl(EDP)_2} \quad (6)$$

Complex of Cobalt. Reaction of cobalt(III) acetylacetonate with ethoxydiethylaluminum in the presence of ethylenebis(diphenylphosphine) gave a red complex, $HCo(EDP)_2$. The infrared spectrum was identical with that of a sample obtained by the reduction of $CoCl_2(EDP)_2$ with $NaBH_4$[18] and showed a Co–H absorption at 1884 cm^{-1}. The gas evolved during the reaction consisted of ethylene and ethane in a ratio of 4:6.

Experimental Section

Reagents. Ethylenebis(diphenylphosphine) was prepared by the method of Hewertson.[19] Iron(III) acetylacetonate and cobalt(III) acetylacetonate were recrystallized from toluene. Ethoxydiethylaluminum was prepared by the reaction of triethylaluminum with ethanol in *n*-pentane. Solvents were refluxed over Na-K amalgam prior to distillation under argon atmosphere. All the preparations were carried out under argon atmosphere.

Preparation of $Fe(EDP)_2\cdot C_2H_4$ (1a and 1b). A solution of 15 ml (100 mmoles) of ethoxydiethylaluminum in 100 ml of ethyl ether was added to a dispersed solution of 5.3 g (15 mmoles) of iron(III) acetylacetonate and 11.9 g (30 mmoles) of ethylenebis(diphenylphosphine) in 250 ml of ether with stirring at 0° for 2.5 hr. Additional stirring was continued for 1 hr at room temperature. Red crystals (**1a**) that precipitated were separated by filtration and washed with 70 ml of ethyl ether. The yield of the crystals was 11.2 g (85%), mp 164°: ν_{max}^{Nujol} 3047, 3019, 1584, 1431, 1162, 1080, 876, 819, 795, 739, 696 cm^{-1}.

Anal. Calcd for $C_{54}H_{52}FeP_4$: C, 73.64; H, 5.95. Found: C, 73.19; H, 5.90.

Repeated recrystallization from benzene–ethyl ether gave violet crystals **1b**, mp 170–171° dec: ν_{max}^{Nujol} 3054, 3016, 1584, 1433, 1166, 1090, 873, 801, 774, 735, 693 cm^{-1}.

Anal. Calcd for $C_{54}H_{52}FeP_4$: C, 73.64; H, 5.95; mol wt, 880. Found: C, 73.58; H, 6.03; mol wt, 840 (cryoscopy, 0.38 mole % in benzene). The gas evolved during the reaction consisted of 7% ethylene, 76% ethane, and 17% butane.

A solution of 0.550 g (0.62 mmole) of **1a** and 0.012 g (0.03 mmole) of ethylenebis(diphenylphosphine) in 15 ml of benzene was allowed to stand overnight. Addition of ethyl ether to the concentrated solution gave **1b** in 75% yield. The same treatment of **1a** in the absence of ethylenebis(diphenylphosphine) resulted in recovery of **1a**.

Reaction of $Fe(EDP)_2\cdot C_2H_4$ with Iodine. A solution of 0.164 g (0.64 mmole) of iodine in 5 ml of benzene was added at 4° to a stirred solution of 0.564 g (0.64 mmole) of **1b** in 20 ml of benzene in a sealed system. The evolved gas was analyzed by gas chromatography and identified as ethylene (12.2 ml at STP, 85%). The mass spectrum of the gas was identical with that of ethylene. A yellow precipitate was filtered off and washed with toluene to give 0.412 g (91% yield) of the complex.

Anal. Calcd for $C_{26}H_{24}FeI_2P_2$: C, 44.01; H, 3.39; I, 35.87. Found: C, 43.95; H, 3.37; I, 35.4.

The infrared spectrum was identical with that of an authentic sample prepared by the reaction of $FeI_2(H_2O)_n$ with ethylenebis(diphenylphosphine). The complex is very slightly soluble in benzene and toluene. From the filtrate 0.172 g (70%) of ethylenebis(diphenylphosphine), mp 143°, was obtained.

Preparation of $HFe(C_6H_4PPh\cdot CH_2CH_2\cdot PPh_2)(EDP)$ (2). Method A. A stirred solution of 0.490 g (0.56 mmole) of **1b** in 15 ml of benzene was irradiated by a 220-W mercury lamp for 3 hr at room temperature. The color of the solution changed from dark red to

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(17) J. Chatt and R. G. Hayter, *ibid.*, 6017 (1963).

(18) A. Sacco and R. Ugo, *ibid.*, 3274 (1964).

(19) W. Hewertson and H. R. Watson, *ibid.*, 1490 (1962).

transparent red. Evolved gas was analyzed by gas chromatography and mass spectroscopy, and identified as ethylene (12.0 ml at STP, 96%). The reaction mixture was concentrated under reduced pressure, and 10 ml of ethyl ether was added. After removal of a small amount of a decomposed product by filtration, 10 ml of *n*-pentane was added to the filtrate to give 0.391 g (82%) of orange-brown crystals which were recrystallized from benzene–ethyl ether, mp 179–180°.

Anal. Calcd for $C_{52}H_{48}FeP_4$: C, 73.24; H, 5.68; mol wt, 852. Found: C, 73.20; H, 5.77; mol wt 832 (cryoscopy, 0.84 mole % in benzene).

Method B. To a solution of 0.980 g (1.11 mmoles) of **1b** in 20 ml of toluene was added 3 ml of the mother liquor obtained in the preparation of **1a**. Ether contained in the mixture was removed under reduced pressure and the resultant solution was heated at 70° for 20 min. The solution was concentrated and 50 ml of *n*-pentane was added. Orange-brown crystals (0.734 g, 77%) were deposited. Evolution of ethylene (24.5 ml at STP) was also observed in this reaction.

The same treatments of **1a** as described in methods A and B afforded **2** with liberation of ethylene.

Reaction of $HFe(C_6H_4PPh\cdot CH_2CH_2\cdot PPh_2)(EDP)$ with Iodine. A solution of 0.152 g (0.60 mmole) of iodine in 5 ml of benzene was added to a stirred solution of 0.501 g (0.58 mmole) of **2** in 5 ml of benzene. A gas buret connected to the reaction flask showed no evolution of gas. After addition of 10 ml of *n*-pentane, a yellow precipitate (0.40 g, 95% yield) was filtered off. It was identified as $FeI_2(EDP)$ by means of infrared spectroscopy and elemental analysis. From the filtrate, 0.14 g (61% yield) of ethylenebis(diphenylphosphine) was obtained.

Reaction of $HFe(C_6H_4PPh\cdot CH_2CH_2\cdot PPh_2)(EDP)$ with Hydrogen Chloride. An ethereal solution (5.5 ml) containing 0.52 mmole of hydrogen chloride was added to a solution of 0.445 g (0.52 mmole) of **2** in 10 ml of xylene at −15°. A violet precipitate was filtered off and dissolved in benzene. After filtration, ethyl ether was added to the filtrate. Purification of the resultant precipitate was repeated to give 0.29 g (63% yield) of the violet complex, mp 209° dec.

Anal. Calcd for $C_{52}H_{49}ClFeP_4$: C, 70.23; H, 5.51; Cl, 3.99. Found: C, 70.31; H, 5.63; Cl, 3.89.

Reaction of $HFe(C_6H_4PPh\cdot CH_2CH_2\cdot PPh_2)(EDP)$ with Deuterium Chloride. An ethereal solution containing 0.83 mmole of deuterium chloride (deuterium content 85%) was added at −30° to a solution of 0.716 g (0.84 mmole) of **2** in 15 ml of toluene. Purification of the product was conducted in the same manner as described in the reaction of **2** with hydrogen chloride. A peak height ratio of an Fe–H signal to a $>PCH_2CH_2P<$ signal in its nmr spectrum was measured. From a comparison with the ratio of the nondeuterated complex, it was determined that 80% of the deuterium atoms was used for the formation of the Fe–D bond. The deuterium content of the ligands was determined as follows. The deuterated complex in benzene was decomposed with excess aqueous hydrogen chloride and the benzene layer concentrated. Recrystallization from 1-propanol gave ethylenebis(diphenylphosphine) in 89% yield. The ratio of an isotope peak P_{M+1} to a parent peak P_M in its mass spectrum was compared with that of the nondeuterated one. It was concluded that 10.5% of the deuterium atoms was present in ethylenebis(diphenylphosphine).

Preparation of $H_2Fe(EDP)_2\cdot C_6H_6$. Method A. Hydrogen was bubbled through a stirred solution of 3.6 g (4.2 mmoles) of **2** in 70 ml of benzene at 70° for 2 hr, causing the solution to become yellow. After filtration, addition of 150 ml of *n*-heptane to the filtrate afforded 2.9 g (81% yield) of pale yellow crystals which were recrystallized from benzene–*n*-heptane.

Anal. Calcd for $C_{58}H_{56}FeP_4$: C, 74.68; H, 6.03. Found: C, 74.68; H, 6.05.

The same reaction in toluene and xylene gave $H_2Fe(EDP)_2\cdot 2C_7H_8$ and $H_2Fe(EDP)_2\cdot C_8H_{10}$, respectively.

Anal. Calcd for $C_{66}H_{66}FeP_4$: C, 76.40; H, 6.46. Found: C, 76.30; H, 6.40. Calcd for $C_{60}H_{60}FeP_4$: C, 74.79; H, 6.20. Found: C, 75.00; H, 6.29.

Method B. Hydrogen was bubbled through a solution of 2.1 g (2.4 mmoles) of **1b** in 60 ml of benzene at 60° for 8 hr. The same treatment as described in method A gave 1.34 g (68% yield) of yellow crystals. The hydrocarbons evolved in this reaction consisted of 95% ethylene and 5% ethane.

The same complex was obtained by means of ultraviolet irradiation of **1b** at room temperature.

Reaction of $H_2Fe(EDP)_2\cdot C_6H_6$ with Iodine. A solution of 0.210 g (0.83 mmole) of iodine in 10 ml of toluene was added dropwise to 0.694 g (0.74 mmole) of the iron dihydride in 20 ml of toluene. A gas buret showed an evolution of 18.5 ml (98%) of hydrogen. A yellow precipitate of $FeI_2(EDP)$ was filtered off. Gas chromatographic analysis showed that the filtrate contained 58.6 mg (100%) of benzene.

Reaction of $HFe(C_6H_4PPh\cdot CH_2CH_2\cdot PPh_2)(EDP)$ with Ethylene. A solution of 0.680 g (0.80 mmole) of the complex in 10 ml of benzene was shaken for 5 hr at 80° under ethylene pressure (60 kg/cm²). The resultant mixture was concentrated and addition of ether gave 0.478 g (68%) of a violet complex, mp 170° dec. The infrared spectrum was identical with that of **1b**.

Anal. Calcd for $C_{54}H_{52}FeP_4$: C, 73.64; H, 5.95. Found: C, 73.79; H, 6.00.

Preparation of $HCo(EDP)_2$. A solution of 5.5 ml of ethoxydiethylaluminum in 10 ml of benzene was added at 6° to a solution of 1.78 g (5 mmoles) of cobalt(III) acetylacetonate and 5.52 g (14 mmoles) of ethylenebis(diphenylphosphine) in 40 ml of benzene. Addition of ethyl ether to the filtrate gave a red precipitate, which was recrystallized from benzene–*n*-hexane, mp 268° dec.

Anal. Calcd for $C_{52}H_{49}CoP_4$: C, 72.89; H, 5.77; P, 14.46. Found: C, 72.97; H, 5.91; P, 14.42.